COAL DESULFURIZATION THROUGH REVERSE MICELLE BIOCATALYSIS PROCESS

by Kwang-Il Lee and Teh Fu Yen

University of Southern California

Department of Civil and Environmental Engineering

Los Angeles, California 90089-0231

ABSTRACT

A novel bioprocess using micelle biocatalysis has been attempted to minimize several disadvantages of conventional microbial coal desulfurization scale-up processes. The reverse micelle biocatalysis process consists of a water-immiscible organic medium, a surfactant, an aqueous phase and sulfur-oxidizing bacteria or enzymes. This process has been successful for removing sulfur from bituminous coal (Illinois coal #5). The preliminary results showed that coal desulfurization through the use of cell-free enzyme extracts of Thiobacillus ferrooxidans ATCC 19859 was better than that of bacteria itself. The use of enzymes has shown potential for commercial coal desulfurization processes as well. This same process is being applied to the thermophillic bacteria Sulfolobus acidocaldarius ATCC 33909. The implications of these experimental results will be discussed, including a hypothetical mechanism using reverse micelle biocatalytical process for coal desulfurization

INTRODUCTION

Since coal utilization as an alternative energy resource is associated with SO_2 emission, causing acid rain and acid fog during stages in the combustion process, there has been a great interest in the desulfurization of coals.

Microbial desulfurization methods are given great amounts of attention because biological removal of sulfur compounds prior to combustion of coals requires low capital and operating costs. Several researchers have demonstrated the feasibility of sulfur removal from pulverized coals by sulfur-oxidizing bacteria. However, this bacterial desulfurization process has not yet been applied on

a commercial scale. This is partically due to the fact that the reaction rate in the bacterial process in comparatively slow, and the microbial cells must be in physcial contact with pyrite to decompose it[1,2]. In order to overcome these barriers, a new desulfurization process is needed.

During the last decade, there has been a rapid growth of the application of biocatalysts (whole cell, purified enzymes and cell organelles) in non-aqueous media. Recent research has revealed that the reverse micellar system -- solvent/surfactant/water -- affords protein solubilization and enzymatic chemical reactions[3,4,5]. Of special interest is the reversed micelle solution (oil/nonionic surfactant/water) which may generate large swollen micelles (globules). The "water pools" of the reversed micelle created by large head groups of the non-ionic surfactants might be used as a "microreactor."

The objective of this work is directed not only to investigate catalytic oxidation of ferrous ion by biocatalysts (bacteria and cell-free enzyme extracts) entrapped in the water pools of the reversed micellar system, but also to provide feasibility of sulfur removal from coal. We will describe here our preliminary results on the iron oxidation via reverse micelle biocatalysis, and on bituminous coal desulfurization.

EXPERIMENTAL

Pure cultures, Thiobacillus ferrooxidans ATCC 19859 and Sulfolobus acidocaldarius ATCC 33909, were obtained from the American Type Culture Collections and routinely maintained[6,7]. Cells were harvested after they were four days old, suspended in distilled water (pH 2.6 with H_2SO_4), and allowed to stand in the refrigerator. The resulting supernatant fluid was carefully collected, brought to a volume of 30 ml with distilled water (pH 2.8), centrifuged and stored in the refrigerator. 10 ml of stored cell suspensions (0.02 g/ml, dry weight) were sonicated in glycine-SO_4 buffer solution (pH 2.8) for one hour so that cell-free enzyme extracts were prepared.

The reversed micellar system included 0.01% nonionic surfactants (Tween 80) in mineral oil (light) (wt/vol) and 1% water phase (vol/vol). The appropriate rates of blowing air in the reversed micellar system were 40 ml m^{-1} at room temperature.

To measure a change of concentration of ferrous ion in the reversed micelle, the ferrous oxidation measurement described by Tamura et al.[8] was adopted. A stable complex of Fe^{2+} having color density by 1,10-phenanthroline assay was determined at 510 nm with the spectrophotometer (Figure 1).

Table 1. Sulfur content of Illinois coal #5

	PYRITIC %	SULFATIC %	ORGANIC %	TOTAL %
SULFUR	1.82	0.03	2.50	4.35

For this study, an Illinois #5 coal sample was collected from the Burning Stat #4 mine in Illinois. This sample was reported to hold 4.35% total sulfur (Table 1). An Illinois coal #5 was crushed and ground to 100 mesh. The obtained coal powder was slowly poured into the mineral oil containing 0.01% non-ionic surfactant (wt/vol). Then, bacteria and respective media (pH 2.4) were added into the organic phase. The mixed multiphase solution was sonicated and vigorously agitated. After incubation, coal particles were collected by centrifuge and washed with hexane and hot water to remove possible oil associated with the coal particles. The washed coal samples were dried and the content of total sulfur was assessed.

RESULTS & DISCUSSION

The iron assay at 510 nm shows a significant decrease of Fe^{2+} ion complex in the reverse micellar system containing the cell-free enzyme extracts of T. ferrooxidans (Figure 2). The Fe^{2+} level was rapidly dropped during the initial one hour; this could be due to enzymatic compounds responsible for iron oxidation entrapped in the water core of the reversed micelle. Such compounds could be a copper protein, rusticyanin and a Fe (II)-oxidizing enzyme from T. ferrooxidans. The result that iron could be oxidized by reversed micelle biocatalyst would support a feasibility of this system for the coal desulfurization process.

Figure 3 shows the data of total sulfur removal by the reverse micelle system. It was observed that there was about 13% total sulfur loss in coals (control) washed with solvent hexane and hot water, when comparing them with raw Illinois coal. The reason for that could be dissolution of elemental sulfur present in coal by solvent and hot water. It was positively observed that sulfur was removed from coal by the sulfur-oxidizing bacteria in the reverse micelle system. Remarkably, more than 37% of the total sulfur removal was found in the coals treated during a 24 hour period with the cell-free enzyme extracts reverse micelle system. It should be pointed out that the desulfurization reaction time by the cell-free enzyme extracts was comparatively very short. Also, the rate of sulfur removal by the cell-free enzyme extracts of Thiobacillus ferrooxidans was much higher than that of the bacteria. We therefore intrepret the preliminary results as showing that mineral oil/non-ionic surfactant/water allow protein solubilization and catalytic reaction. Hence, a reverse micelle biocatalysis seems to be a promising coal desulferization process. Further studies are being conducted with the thermophilic bacteria S. acidocaldarius. The implications of these results will be addressed.

ACKNOWLEDGEMENTS

We acknowledge Energy and Environmental Labs, Inc. for partial support.

REFERENCES

1. Andrews, G.W. and J. Maczuga, "Bacterial Coal Desulfurization," the 4th Symposium on Biotechnology in Energy Production and Conversion, Gatlinburg, Tenessee, May 11-14, (1982).

2. Hoffmann, M.R., B.C. Faust, F.A. Panda, H.H. Koo and H.M. Tsuchiya, "Kinetics of the Removal of Iron Pyrite from Coal by Microbial Catalysis," Appl. Environ. Microbiol., 42, 259-271 (1981).

3. Luisi, P.L. and C. Laane, "Solubilization of Enzymes in Apolar Solvents via Reverse Micelles," TIBTECH, 153-161, June (1986).

4. Kadam, K.L., "Reverse Micelles as a Bioseparation Tool," Enzyme Microb. Technol., 8, 266-273, (1986).

5. Goklen, K.E. and T.A. Hattan, "Protein Extraction Using Reverse Micelles," Biotechnology Progress, 1(1), 69-74, 1985.

6. Silverman, M.P. and D.G. Lundgren, "Studies on the Chemoautotropic Iron Bacterium Ferrobacillus Ferrooxidans," J. Bacteriol., 77, 641-647 (1959).

7. Kargi, F. and J.M. Robinson, "Removal of Sulfur Compounds from Coal by the Thermophilic Organism Sulfolobus acidocaldarius," Appl. Environ. Microbiol., 44, 878-883, (1982).

8. Tamura, H., K. Goto and M. Nagayama, "Spectrophotometric Determination of Iron (II) with 1,10-phenanthraline in the Presence of Large Amounts of Iron (III)," Talanta, 21, 314-318 (1974).

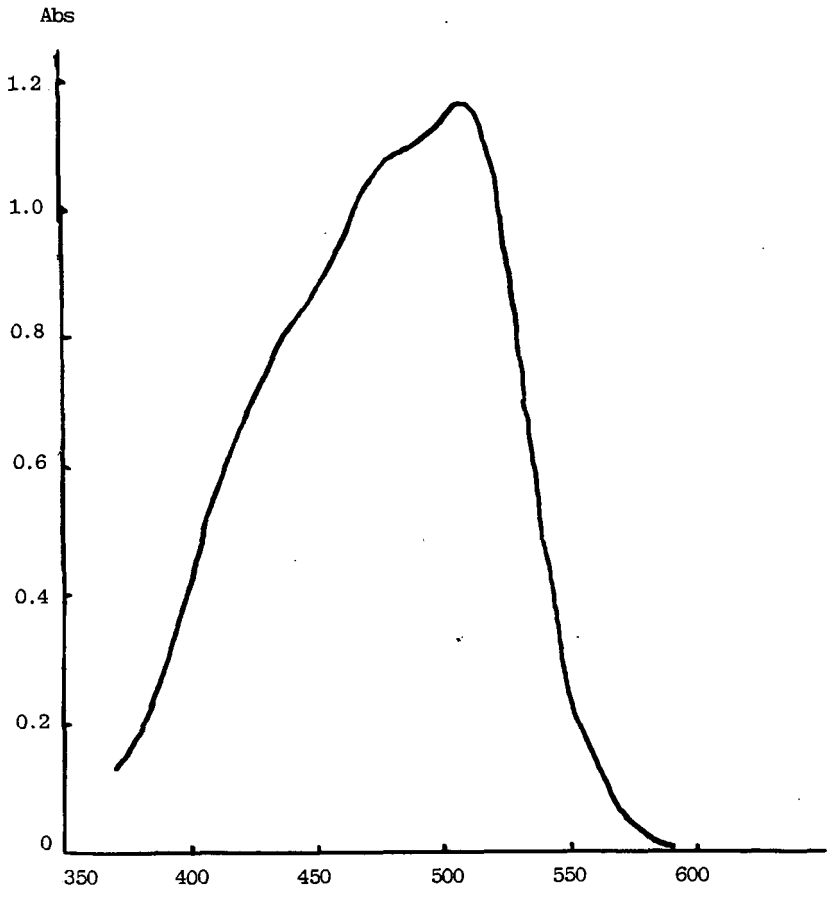
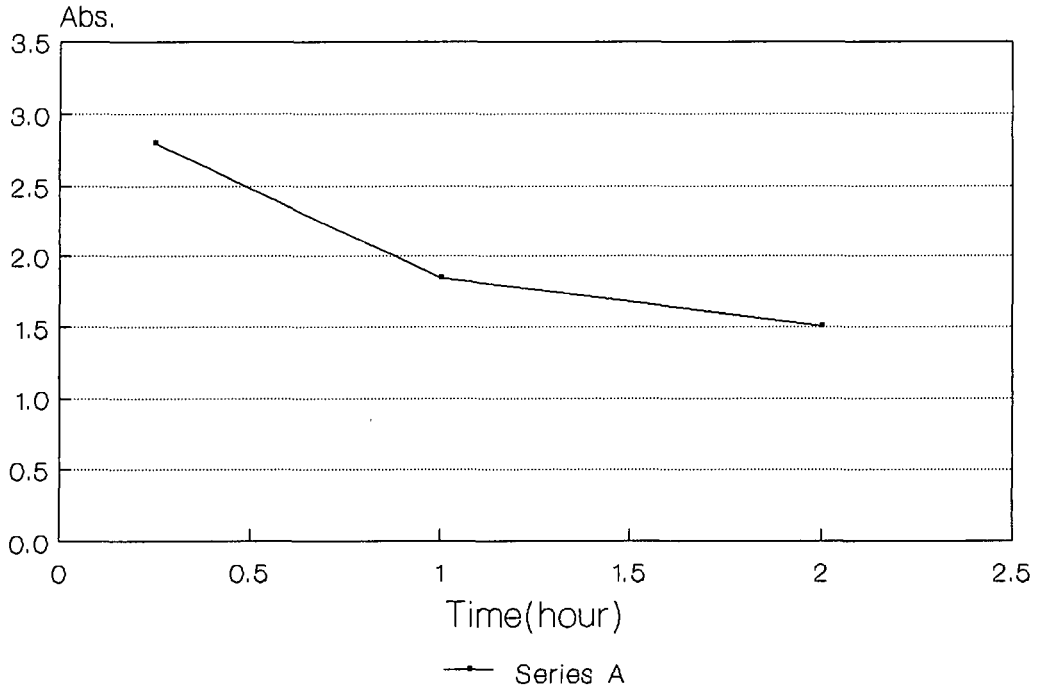


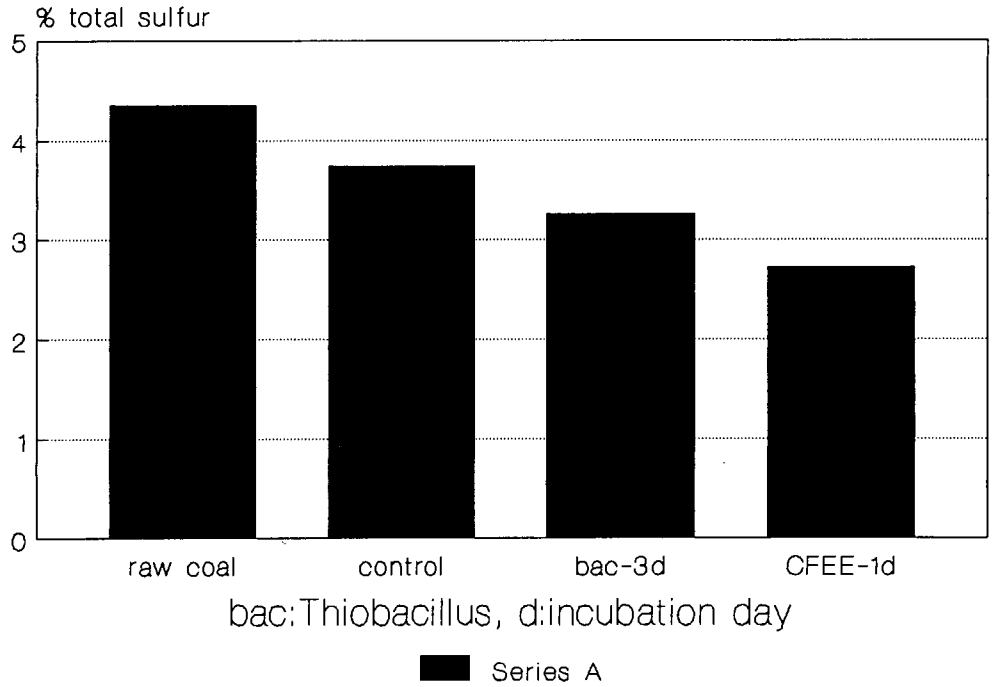
Figure 1. Absorption spectrum of 1,10-phenanthroline-iron complex extracted from reverse micelle system.

Figure 2. Iron oxidation via reverse micelle biocatalysts.



Cell-free enzyme extract of Thiobacillus

Figure 3. Coal desulfurization via reverse micelle biocatalysts.



CFEE:cell-free enzyme extract